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(54) CATALYST FOR PRODUCTION OF METHACRYLIC ACID AND PRODUCTION OF METHACRYLIC ACID

(57)Abstract:

PROBLEM TO BE SOLVED: To oxidize methacrolein by vapor phase catalytic oxidation with molecular oxygen and to produce methacrylic acid in a high yield by using a catalyst produced while specifying the amount of ammonium radicals in one solution in a specified mixed solution and the amount of ammonium radicals in the mixed solution.

SOLUTION: The catalyst used in the production of methacrylic acid by the vapor phase catalytic oxidation of methacrolein with molecular oxygen has a composition of the formula $\text{PaMo}_b\text{V}_c\text{Cu}_d\text{XeYfZgOh}$ and is produced by mixing a solution (A) containing at least molybdenum, phosphorus and vanadium with a solution (B) containing an ammonia compound and further mixing the resulting mixed solution (AB) with a solution (C) containing the element Z. The amount of ammonium radicals in the solution A is ≤ 1.5 mol based 12 mol molybdenum atoms in the solution A and the amount of ammonium radicals in the solution AB is 6-17 mols based 12 mol molybdenum atoms in the solution AB.

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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

[Claim(s)]

[Claim 1] the following type (1) used when carrying out gas phase catalytic oxidation of the methacrolein by molecule-like oxygen and manufacturing methacrylic acid

PaMobVcCudXeYfZgOh (1)

the inside of a formula, P and Mo, V, Cu, and O -- respectively -- a phosphorus and molybdenum -- Vanadium, copper, and oxygen are shown and X Antimony, bismuth, arsenic, At least one kind of element chosen from the group which consists of germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron is shown. Y Iron, zinc, chromium, magnesium, a tantalum, Cobalt, manganese, At least one kind of element chosen from the group which consists of barium, gallium, cerium, and lanthanum is shown, and Z shows at least one kind of element chosen from the group which consists of potassium, rubidium, caesium, and thallium. a, b, c, d, e, f, g, and h express the atomic ratio of each element, and are $a = 0.5-3$, $c = 0.01-3$, $d = 0.01-2$, $e = 0-3$, $f = 0-3$, and $g = 0.01-3$ at the time of $b = 12$. h is the atomic ratio of oxygen required to satisfy the valence of each of said component. It is the catalyst which has the presentation expressed. The solution or slurry (B liquid) containing the solution or slurry (A liquid) which contains molybdenum, a phosphorus, and vanadium at least, and an ammonia compound is mixed. In the catalyst manufactured by the manufacture method including the process which mixes the solution or slurry (C liquid) which contains Z element in the obtained mixed liquor or mixed slurry (AB mixed liquor) The catalyst for methacrylic acid manufacture characterized by for the quantity of the ammonium root in A liquid having been 1.5mol or less to 12mol of molybdenum atoms in A liquid, and manufacturing the quantity of the ammonium root in AB mixed liquor as 6-17mol to 12mol of molybdenum atoms in AB mixed liquor.

[Claim 2] The catalyst for methacrylic acid manufacture according to claim 1 characterized by mixing copper or Y element into AB mixed liquor beforehand before mixing AB mixed liquor and C liquid.

[Claim 3] The manufacture method of the methacrylic acid using the catalyst for methacrylic acid manufacture according to claim 1 or 2.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the catalyst (only henceforth the catalyst for methacrylic acid manufacture) for carrying out gas phase catalytic oxidation of the methacrolein by molecule-like oxygen, and manufacturing methacrylic acid, and the manufacture method of methacrylic acid.

[0002]

[Description of the Prior Art] As how to mix two or more kinds of mixed solutions which contain a catalyst component element among the manufacture methods of the catalyst for methacrylic acid manufacture known conventionally, For example, the method indicated to JP,H4-182450,A, JP,H5-31368,A, JP,H7-185354,A, JP,H8-157414,A, JP,H8-196908,A, etc. is mentioned. In particular, to JP,H5-31368,A, the liquid which contains molybdenum, a phosphorus, and vanadium at least, and the liquid containing an ammonia compound are mixed, and the manufacture method of the catalyst for methacrylic acid manufacture which mixes the liquid which contains a caesium element in the obtained mixed liquor is indicated to it.

[0003] Moreover, in JP,H9-290162,A, the method of adding nitric acid or aqueous ammonia and adjusting is indicated in pH of the raw material solution containing all the catalyst raw materials.

[0004]

[Problem(s) to be Solved by the Invention] However, the methacrylic acid yield of the catalyst manufactured using the mixed method and the pH adjustment method of such a conventional catalyst raw material is not necessarily enough as a catalyst for industry, and the present condition is that improvement is desired further.

[0005] Therefore, this invention aims at offering the manufacture method of a catalyst and methacrylic acid that gas phase catalytic oxidation of the methacrolein is carried out by molecule-like oxygen, and methacrylic acid can be manufactured with high yield.

[0006]

[Means for Solving the Problem] This invention is the following type (1) used when carrying out gas phase catalytic oxidation of the methacrolein by molecule-like oxygen and manufacturing methacrylic acid.

PaMobVcCudXeYfZgOh (1)

the inside of a formula, P and Mo, V, Cu, and O -- respectively -- a phosphorus and molybdenum -- Vanadium, copper, and oxygen are shown and X Antimony, bismuth, arsenic, At least one kind of element chosen from the group which consists of germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron is shown. Y Iron, zinc, chromium, magnesium, a tantalum, Cobalt, manganese, At least one kind of element chosen from the

group which consists of barium, gallium, cerium, and lanthanum is shown, and Z shows at least one kind of element chosen from the group which consists of potassium, rubidium, caesium, and thallium. a, b, c, d, e, f, g, and h express the atomic ratio of each element, and are $a = 0.5-3$, $c = 0.01-3$, $d = 0.01-2$, $e = 0-3$, $f = 0-3$, and $g = 0.01-3$ at the time of $b = 12$. h is the atomic ratio of oxygen required to satisfy the valence of each of said component. It is the catalyst which has the presentation expressed. The solution or slurry (B liquid) containing the solution or slurry (A liquid) which contains molybdenum, a phosphorus, and vanadium at least, and an ammonia compound is mixed. In the catalyst manufactured by the manufacture method including the process which mixes the solution or slurry (C liquid) which contains Z element in the obtained mixed liquor or mixed slurry (AB mixed liquor) It is the catalyst for methacrylic acid manufacture characterized by for the quantity of the ammonium root in A liquid having been 1.5mol or less to 12mol of molybdenum atoms in A liquid, and manufacturing the quantity of the ammonium root in AB mixed liquor as 6-17mol to 12mol of molybdenum atoms in AB mixed liquor.

[0007]

[Embodiment of the Invention] The catalyst of this invention has the presentation expressed with said formula (1). It is indispensable to include the following two processes in manufacture of the catalyst of this invention.

(I) Process which mixes "the solution or slurry" which is called A liquid, and which contains molybdenum, a phosphorus, and vanadium at least, and "the solution or slurry" which is called B liquid, and containing an ammonia compound, and obtains the mixed solution or slurry of A liquid and B liquid called AB mixed liquor.

(II) Process which manufactures the solution or slurry which contains a catalyst precursor by mixing the solution or slurry which contains said Z element called C liquid in AB mixed liquor.

[0008] Moreover, in this invention, the quantity of the ammonium root in A liquid shall be 1.5mol or less to 12mol of molybdenum atoms in A liquid, and shall be 1mol or less preferably. Moreover, the quantity of the ammonium root in AB mixed liquor shall be 6-17mol to 12mol of molybdenum atoms in AB mixed liquor, and shall be 7-15mol preferably.

[0009] Moreover, the slurry to which the whole quantity also suspended in part the solution which restriction in particular will not have if, as for the state of A liquid, B liquid, AB mixed liquor, and C liquid, the catalyst raw material is included in liquid, and the catalyst raw material dissolved in the solvent completely in the solvent is sufficient. As a solvent, water is desirable here.

[0010] Thus, the solution or slurry containing the obtained catalyst precursor is made into the catalyst for methacrylic acid manufacture desiccation and by subsequently calcinating.

[0011] Although it is not clear about the mechanism whose catalyst performance improves by adopting such a manufacture method, it is controlling the ammonium root in the mixed order of a catalyst raw material, and A liquid and AB mixed liquor to a specific amount. Methacrylic acid is presumed because the crystal structure which can be acquired with high yield is formed.

[0012] It explains in more detail about the manufacture method of the catalyst of this invention

hereafter.

(Preparation of A liquid) After making a solvent dissolve or suspend the catalyst raw material of molybdenum, a phosphorus, and vanadium at least, 80-150 degrees C, A liquid is 90-130 degrees C preferably, carries out heating churning preferably for 1 to 12 hours, and prepares this for 0.5 to 24 hours. A catalyst with the high activity of a methacrylic acid manufacture reaction is acquired because cooking temperature shall be 80-150 degrees C. Moreover, by carrying out heat time in 0.5 hours or more, the reaction of catalyst raw materials can fully be advanced.

[0013] A liquid is the solution or slurry which included the catalyst raw material of molybdenum, a phosphorus, and vanadium at least, and may include the catalyst raw material of the element except Z element besides molybdenum, a phosphorus, and vanadium.

[0014] As a catalyst raw material used for manufacture of A liquid, the oxide of each element, nitrate, carbonate, ammonium salt, etc. can be used, choosing them suitably. For example, although the raw material which does not contain ammonium roots, such as molybdenum trioxide and molybdic acid, as a raw material of molybdenum is suitable Can use it, if various ammonium molybdate, such as Para ammonium molybdate, JIMORIBUDEN acid ammonium, and tetra-ammonium molybdate, is also little, and as a phosphorus raw material

Orthophosphoric acid, phosphorus pentoxide, ammonium phosphate, etc. can be used, and vanadium pentoxide, ammonium metavanadate, etc. can be used as a raw material of vanadium. Moreover, heteropolyacids, such as molybdophosphoric acid, a molybdo

BANADORIN acid, and ammonium phosphomolybdate, can also be used as a raw material of molybdenum, a phosphorus, and vanadium.

[0015] It is important for the quantity of the ammonium root in A liquid to consider it as 1.5mol or less to 12mol of molybdenum atoms in liquid, and in order to raise the yield of methacrylic acid further, it is desirable to consider it as 1mol or less. The quantity of the ammonium root in A liquid can be adjusted by the amount of the catalyst raw material used containing an ammonium root.

[0016] (Preparation of B liquid) B liquid is the solution or slurry containing an ammonia compound, to a solvent, is dissolved or suspended and prepares an ammonia compound. It is more desirable to contain in B liquid, as long as the catalyst raw material of elements other than said Z element is not the whole quantity besides an ammonia compound, either, but not to include any components other than an ammonia compound. An ammonia compound is the compound or ammonia containing ammonium here, for example, aqueous ammonia, ammonium nitrate, an ammonium carbonate, an ammonium hydrogencarbonate, etc. are mentioned.

[0017] The quantity of the ammonia compound in B liquid is quantity that the quantity of the ammonium root in AB mixed liquor which mixed A liquid and B liquid becomes 6-17mol to 12mol of molybdenum atoms in liquid, and the quantity which is preferably set to 7-15.

[0018] (Preparation of C liquid) C liquid is the solution or slurry containing said Z element, at least, to a solvent, is dissolved or suspended and prepares the catalyst raw material of Z

element. It is more desirable not to include these as much as possible, although the catalyst raw material of elements other than Z element may be included in C liquid. Moreover, it is desirable that an ammonia compound is not included as much as possible in C liquid. Nitrate of each element, carbonate, a hydroxide, etc. can be used as a catalyst raw material of C liquid, choosing them suitably. For example, as a raw material of caesium, nitric acid caesium, cesium carbonate, cesium hydroxide, etc. can be used.

[0019] (Preparation of AB mixed liquor) In this invention, A liquid and B liquid are mixed and AB mixed liquor is obtained. Especially the mixed method of A liquid and B liquid can use the methods that the method of adding B liquid to the container into which it was not limited, for example, A liquid went, the method of adding A liquid to the container with which B liquid entered, the method of slushing A liquid and B liquid into a container simultaneously, etc. are arbitrary. To obtain AB mixed liquor, you may operate heating aging etc. suitably. In order to acquire a catalyst with high activity, as for the temperature of A liquid at the time of mixing, and B liquid, it is desirable respectively that it is 70 degrees C or less, and it is desirable. [of especially 60 degrees C or less]

[0020] You may add the catalyst raw material except Z component to what mixed A liquid and B liquid further. Thus, as long as it is the catalyst raw material of elements other than Z element contained in the catalyst presentation shown by said formula (1) as a catalyst raw material to add, any are sufficient, and the additional method may add a catalyst raw material as it is, and may add it in the state of a solution or suspension.

[0021] (Mixing of AB mixed liquor and C liquid) In this invention, aforementioned AB mixed liquor and C liquid are mixed. Although the method in particular of mixing AB mixed liquor and C liquid is not limited, the method of adding C liquid to the container containing AB mixed liquor, the method of adding AB mixed liquor to the container with which C liquid entered, the method of slushing AB mixed liquor and C liquid into a container simultaneously, etc. are mentioned, for example.

[0022] In this invention, when mixing AB mixed liquor and C liquid, it is more desirable to mix AB mixed liquor, copper, or said Y element beforehand, and to mix the obtained mixed liquor and C liquid. Here, copper or said Y element has especially the desirable thing for which a solvent is made to dissolve or suspend these catalyst raw materials, and they are added to it. When adding this copper or said Y element, the catalyst raw material of elements other than Z element may also be set and added, but it is more desirable not to add these as much as possible at this time. Moreover, also as for an ammonia compound, it is desirable not to add as much as possible at this time. Nitrate of each element, carbonate, a hydroxide, etc. can be used as a catalyst raw material of copper and Y element, choosing them suitably. For example, copper nitrate, copper oxide, etc. can be used as a copper raw material. The method in particular of mixing the mixed liquor obtained by having mixed AB mixed liquor, copper, or said Y element and C liquid is not limited. Thus, to the obtained solution or slurry which mixed AB mixed liquor and C liquid at least, you may operate heating aging etc. suitably. Although the temperature in particular of both the liquid at the time of mixing is not limited, 100 degrees

C or less are desirable.

[0023] (Desiccation and calcination) If the solution or slurry which does in this way and includes all the catalyst raw materials is obtained, this solution or slurry will be dried and the dry matter of a catalyst precursor will be obtained. It is possible to use the desiccation method of this time versatility, for example, an evaporation-to-dryness method, a spray drying method, a drum dry technique, a flash drying method, etc. can be used. Neither the model of dryer used for desiccation nor the temperature in particular at the time of desiccation is limited, but can obtain the dry matter of the catalyst precursor according to the purpose by changing desiccation conditions suitably.

[0024] Although you may calcinate without fabricating the dry matter of this catalyst precursor, the usually fabricated mold goods are calcinated. Although the shaping method in particular is not limited but the various molding methods of well-known dry type and a wet type can be applied, the method of including and fabricating a carrier etc. is desirable. As the concrete shaping method, tableting shaping, press forming, extrusion, granulation shaping, etc. are mentioned, for example. It is not limited in particular for the form of mold goods, for example, cylindrical, the shape of a ring, and the form of a request of spherical ** can be chosen. In addition, when fabricating, you may add a small amount of well-known additives, for example, graphite, talcs, etc.

[0025] Thus, the dry matter of the obtained catalyst precursor or its mold goods are calcinated, and the catalyst for methacrylic acid manufacture is acquired. In particular the method or calcination conditions to calcinate are not limited, but can apply the well-known treatment method and well-known conditions. Although the optimum conditions of calcination change with the catalyst raw materials, the catalyst presentations, and the methods of preparation to be used, under oxygen content gas circulation of air etc., and/or inert gas circulation, 200-500 degrees C, the usual calcination conditions are 300-450 degrees C preferably, and are 1 to 40 hours preferably for 0.5 hours or more. Inert gas means a gas into which the labile of a catalyst is not reduced here. As such a gas, nitrogen, carbon dioxide gas, helium, argon, etc. are mentioned.

[0026] Thus, when manufacturing methacrylic acid using the manufactured catalyst, the material gas containing methacrolein and molecule-like oxygen is contacted for a catalyst.

Although the methacrolein concentration in material gas is changeable in the large range, 1-20 volume % is suitable, and 3-10 volume % is especially desirable. Although a little impurities, such as water and low-grade saturation aldehyde, may be included in material gas, few [as much as possible] things are desirable. Although it is economical to use air as a molecule-like oxygen source, if required, the air wealth-ized by pure oxygen can also be used. As for especially the molecule-like oxygen concentration in material gas, 0.5-3mol is desirable 0.4-4mol to 1mol of methacroleins. Material gas may add and dilute inert gas, such as nitrogen and carbon dioxide gas, and a steam may be added to material gas. As for the reaction pressure of a methacrylic acid manufacture reaction, from ordinary pressure to several atmospheres are good. Moreover, although reaction temperature can be chosen in 230-450

degrees C, 250-400 degrees C is especially desirable.

[0027]

[Example] Although an example and a comparative example explain this invention still in detail below, this invention is not limited to these examples. The "part" in an example and a comparative example means a weight part. The presentation of the catalyst was calculated from the raw material brewing quantity of the catalyst component. Analysis of the reaction raw material and the product was conducted using gas chromatography. In addition, the conversion of methacrolein, the selectivity of the generated methacrylic acid, and single ***** of methacrylic acid are defined as follows.

the selectivity (%) = $(C/B) \times 100$ methacrylic acid of the conversion (%) = $(B/A) \times 100$ methacrylic acid of methacrolein -- single -- ***** (%) = $(C/A) \times 100$ -- here, the mol of the methacrolein which A supplied -- the mol of the methacrolein to which a number and B reacted -- the mol of the methacrylic acid which a number and C generated -- it is a number.

[0028] [Example 1] 100 copies of molybdenum trioxide, 7.34 copies of 85-weight % phosphoric acid, 4.74 copies of vanadium pentoxides, 0.92 copy of copper oxide, and 0.23 copy of iron oxide were added to 400 copies of pure water, it agitated under flowing back for 5 hours, and A liquid was obtained. The quantity of the ammonium root in A liquid was 0mol to 12mol of molybdenum atoms. After cooling A liquid to 50 degrees C, 37.4 copies of 29-weight % aqueous ammonia which is B liquid was dropped, it agitated for 15 minutes, and AB mixed liquor was obtained. The quantity of the ammonium root in AB mixed liquor was 11mol to 12mol of molybdenum atoms. Next, the solution which dissolved 9.03 copies of nitric acid caesium which is C liquid in 30 copies of pure water was dropped at AB mixed liquor, it agitated for 15 minutes, and slurry was obtained. Thus, heating and agitating the obtained slurry to 101 degrees C, evaporation to dryness was carried out and the obtained solid matter was dried at 130 degrees C for 16 hours. Pressing of this dry matter was carried out, it calcinated at 375 degrees C under air circulation for 10 hours, and the catalyst of the presentation which becomes $P_{1.1}Mo_{12}V_{0.9}Cu_{0.2}Fe_{0.05}Cs_{0.8}$ was acquired. The reaction pipe was filled up with this catalyst and the mixed gas of 10% of oxygen, 30% of a steam, and 55% (volume %) of nitrogen was led methacrolein 5% in reaction temperature [of 285 degrees C], and contact time 3.6 seconds. This result was shown in Table 1.

[0029] [Example 2] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the quantity of the ammonium root in AB mixed liquor so that it might become 6mol to 12mol of molybdenum atoms, by using 24 copies of aqueous ammonia 29weight % as B liquid.

[0030] [Example 3] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the quantity of the ammonium root in AB mixed liquor so that it might become 15mol to 12mol of molybdenum atoms, by using 51 copies of aqueous ammonia 29weight % as B liquid.

[0031] [Example 4] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the quantity of the ammonium root in

AB mixed liquor so that it might become 4mol to 12mol of molybdenum atoms, by 13.6 copies of aqueous ammonia using 29weight % as B liquid.

[0032] [Example 5] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the quantity of the ammonium root in AB mixed liquor so that it might become 20mol to 12mol of molybdenum atoms, by 68 copies of aqueous ammonia using 29weight % as B liquid.

[0033] [Example 6] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the dropping temperature of B liquid into 80 degrees C.

[0034] [Comparative example 1] In an example 1, 13.6 copies of aqueous ammonia is added 29weight % in A liquid, The quantity of the ammonium root in A liquid shall be 4mol to 12mol of molybdenum atoms. The result made to be the same as that of an example 1 was shown in Table 1 except the point of having changed the quantity of the ammonium root in AB mixed liquor so that it might become 11mol to 12mol of molybdenum atoms, by 23.8 copies of aqueous ammonia using B liquid 29weight %.

[0035] [Comparative example 2] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point changed so that the mixed order of B liquid and C liquid might be made reverse, C liquid might be dropped at A liquid and B liquid might be dropped at the mixed liquor.

[0036] [Comparative example 3] In the example 1, the result made to be the same as that of an example 1 was shown in Table 1 except the point changed so that the mixture of B liquid and C liquid might be dropped at A liquid.

[0037] [Example 7] To 400 copies of pure water, 100 copies of molybdenum trioxide, 8.88 copies of 85-weight % phosphoric acid, What dissolved 4.74 copies of ammonium metavanadate, and the second 1.40 copies of copper of nitric acid in ten copies of pure water, The thing, 4.11 copies of 60-weight % arsenic acid aqueous solutions, and 1.00 copies of cerium oxide which dissolved the second 2.34 copies of iron of nitric acid in ten copies of pure water are added, and it agitates at 120 degrees C among an autoclave and under saturated steam for 3 hours. A liquid was obtained. The quantity of the ammonium root in A liquid was 0.7mol to 12mol of molybdenum atoms. After cooling A liquid to 60 degrees C, the solution which dissolved 37.0 copies of ammonium carbonates which are B liquid in 80 copies of pure water was dropped, it agitated for 15 minutes, and AB mixed liquor was obtained. The quantity of the ammonium root in AB mixed liquor was 14mol to 12mol of molybdenum atoms. Next, the solution which dissolved 18.0 copies of GCC acid caesium which is C liquid in 30 copies of pure water is dropped at AB mixed liquor, and it agitates for 15 minutes, and is slurry ****. Thus, heating and agitating the obtained slurry to 101 degrees C, evaporation to dryness was carried out and the obtained solid matter was dried at 130 degrees C for 16 hours. carrying out pressing of this dry matter, and calcinating it at 340 degrees C under air circulation further after 5-hour calcination at 400 degrees C under nitrogen circulation for 10 hours --

P1.3Mo12V0.7Cu0.1Fe0.1As0.3Ce0.1Cs1.6 -- the catalyst of the presentation was acquired.

The result of having reacted on the same conditions as an example 1 is shown in Table 1 using this catalyst except the point of having changed reaction temperature into 290 degrees C.

[0038] [Example 8] 100 copies of molybdenum trioxide, 8.88 copies of 85-weight % phosphoric acid, 4.74 copies of ammonium metavanadate, and 4.11 copies of 60-weight % arsenic acid aqueous solutions were added to 400 copies of pure water, it agitated at 120 degrees C among an autoclave and under saturated steam for 3 hours, and A liquid was obtained. The quantity of the ammonium root in A liquid was 0.7mol to 12mol of molybdenum atoms. After cooling A liquid to 60 degrees C, the solution which dissolved 37.0 copies of ammonium carbonates which are B liquid in 80 copies of pure water was dropped, it agitated for 15 minutes, and AB mixed liquor was obtained. The quantity of the ammonium root in AB mixed liquor was 14mol to 12mol of molybdenum atoms. Next, the thing which dissolved the second 1.40 copies of copper of nitric acid in ten copies of pure water at AB mixed liquor, The solution which dissolved 18.0 copies of GCC acid caesium which is C liquid in 30 copies of pure water after adding the thing and 1.00 copies of cerium oxide which dissolved the second 2.34 copies of iron of nitric acid in ten copies of pure water one by one is dropped, and it agitates for 15 minutes, and is slurry ****. Thus, heating and agitating the obtained slurry to 101 degrees C, evaporation to dryness was carried out and the obtained solid matter was dried at 130 degrees C for 16 hours. carrying out pressing of this dry matter, and calcinating it at 340 degrees C under air circulation further after 5-hour calcination at 400 degrees C under nitrogen circulation for 10 hours -- $P_{1.3}Mo_{12}V_{0.7}Cu_{0.1}Fe_{0.1}As_{0.3}Ce_{0.1}Cs_{1.6}$ -- the catalyst of the presentation was acquired. The result of having reacted on the same conditions as an example 1 is shown in Table 1 using this catalyst except the point of having changed reaction temperature into 290 degrees C.

[0039] [Comparative example 4] In the example 7, the result made to be the same as that of an example 7 was shown in Table 1 except the point changed into the method of slushing A liquid, B liquid, and C liquid into a container simultaneously, and mixing mixing of A liquid, B liquid, and C liquid.

[0040]

[Table 1]

| | 添加順序 ⁽¹⁾ | アンモニウム根比率 | | MAL ⁽³⁾ 転化率(%) | MAA ⁽⁴⁾ 選択率(%) | MAA ⁽⁴⁾ 単収率(%) |
|-------|---------------------|-----------|----------------------|------------------------------|------------------------------|------------------------------|
| | | A液 | AB混合液 ⁽²⁾ | | | |
| 実施例 1 | (A+B)+C | | 11.0 | 83.6 | 82.4 | 68.9 |
| 実施例 2 | (A+B)+C | | 6.0 | 83.0 | 82.8 | 68.7 |
| 実施例 3 | (A+B)+C | | 15.0 | 83.3 | 82.6 | 68.8 |
| 実施例 4 | (A+B)+C | | 4.0 | 80.6 | 83.1 | 68.9 |
| 実施例 5 | (A+B)+C | | 20.0 | 79.8 | 83.4 | 68.6 |
| 実施例 6 | (A+B)+C | | 11.0 | 81.6 | 82.5 | 67.2 |
| 比較例 1 | (A+B)+C | 4.0 | 7.0 | 78.6 | 83.0 | 65.2 |
| 比較例 2 | (A+C)+B | | 11.0 | 77.7 | 83.2 | 64.6 |
| 比較例 3 | A+(B+C) | | 11.0 | 78.3 | 83.0 | 65.0 |
| 実施例 7 | (A+B)+C | 0.7 | 13.3 | 80.3 | 83.5 | 67.1 |
| 実施例 8 | (A+B)+C | 0.7 | 13.3 | 81.2 | 83.6 | 67.9 |
| 比較例 4 | (A+B)+C | 0.7 | 13.3 | 76.5 | 83.4 | 63.8 |

1) 添加順序の欄の記号の意味は次の通り。

(A+B)+C : A液にB液を添加した後にC液を添加する

(A+C)+B : A液にC液を添加した後にB液を添加する

A+(B+C) : A液にB液とC液の混合液を添加する

(A+B)+C : A液、B液およびC液を同時に混合する

2) 添加順序が(A+B)+C以外の場合、AB混合液のアンモニウム根比率はC液を含めた混合液のアンモニウム根比率をいう。

3) MALとはメタクロレインを表す。

4) MAAとはメタクリル酸を表す。

[0041]

[Effect of the Invention] Methacrylic acid can be manufactured with high yield by using the catalyst of this invention.

[Translation done.]